PARABENZOYLDIPHENYLSULPHONE

—AND—

RELATED COMPOUNDS.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

LYMAN C. NEWELL.

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PARABENZOYLDIPHENYLSULPHONE

—AND—

RELATED COMPOUNDS.

I. Introduction.

The primary object in mind when this research was begun was to make and study orthobenzoyldiphenylsulphone

$$C_6H_4<\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix}.$$

This compound was obtained by Remsen and Saunders[1] by the action of benzene and aluminium chloride on the mixed chlorides and on the high melting chloride of orthosulphobenzoic acid. The general plan was to start with toluenesulphone chloride, $C_6H_4<\begin{matrix}CH_3\\SO_2.Cl\end{matrix}$, replace the chlorine by the phenyl group by the Friedel-Crafts reaction, thus passing to tolylphenylsulphone, $C_6H_4<\begin{matrix}CH_3\\SO_2.C_6H_5\end{matrix}$; oxidize the methyl group, and thus make phenylsulphonebenzoic acid, $C_6H_4<\begin{matrix}COOH\\SO_2.C_6H_5\end{matrix}$; then treat this acid or its salt with phosphorus pentachloride to form the corresponding acid chloride, $C_6H_4<\begin{matrix}CO.Cl\\SO_2.C_6H_5\end{matrix}$, which, by the action of benzene and aluminium chloride, would yield benzoyldiphenylsulphone, $C_6H_4<\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix}$.

It was deemed advisable to begin the work in the *para* series, and as the results have been so fruitful, nearly the whole investigation has been confined to this series.

II. Preparation of Material.

The starting-point of this investigation was paratoluenesulphone chloride. The actual substance used was prepared by the usual method, and was a kilogram of the chloride which had accumulated as a residue in the preparation of the ortho analogue. The raw product was washed with cold water, sucked hard on the filter-pump to remove all traces of the liquid ortho chloride, dried, and recrystallized from ordinary ether.

[1] Am. Chem. J., **17**, 362.

III. Paratolylphenylsulphone.

This compound was made by Michael and Adair,[1] in 1878, from benzenesulphonic acid, toluene and phosphorus pentoxide, and also from toluenesulphonic acid, benzene and phosphorus pentoxide; it was made in the same year by Beckurts and R. Otto[2] by the action of toluene and aluminium chloride on benzenesulphone chloride; and by R. Otto,[3] in 1885, from toluenesulphone chloride, benzene, and mercury diphenyl. The products obtained by these different methods melted at 124°–125°, and were either fine white prisms or small rhombohedral plates.

The method employed in this investigation was analogous to that of Beckurts and R. Otto,[4] the only difference being the use of para*toluene*sulphone chloride, which was transformed into paratolylphenylsulphone by *benzene* and aluminium chloride, *i. e.*, by the Friedel-Crafts reaction. The detailed method is as follows: One part paratoluenesulphone chloride is dissolved in an equal weight of warm benzene, and the solution poured into a flask of convenient size, which is attached to a return condenser. The flask is then placed in a water-bath, the temperature of the water raised to about 75°, and powdered aluminium chloride introduced into the flask in small portions until an amount has been added which is equal to three-fourths the weight of the benzene used. The reaction proceeds briskly at 75° until the chloride is almost entirely converted into the paratolylphenylsulphone. When the evolution of hydrochloric acid has ceased, the temperature is raised to 80°, and kept at this point for three-quarters of an hour. The product of the reaction, which is a black, viscous mass is poured into a large volume of warm water, acidified with hydrochloric acid and warmed on the water-bath till all the benzene is driven off. The paratolylphenylsulphone then appears on the surface of the water as small brownish-yellow lumps. It is filtered, washed with warm water, purified by animal charcoal and crystallized from hot ordinary alcohol. The purified product has the form of

[1] Ber. d. chem. Ges., **11**, 116. [2] Ber. d. chem. Ges., **11**, 2068.
[3] Ber. d. chem. Ges., **18**, 249. [4] *Loc. cit.*

hexagonal plates, and melts at 124°–125°. The yield is about ninety-five per cent. of the theoretical amount.

IV. Paraphenylsulphonebenzoic Acid.

This acid was also made by Michael and Adair[1] by oxidizing paratolylphenylsulphone with the calculated amount of potassium permanganate in acetic acid solution, and by boiling the sulphone with potassium permanganate dissolved in a large excess of water. The yield in each case was exceedingly small. The product obtained by both methods crystallized from hot alcohol in fine transparent prisms, which were said to melt above 300° (see page 8).

The methods employed by Michael and Adair were tried and abandoned, because the yield was small and the methods tedious. The sulphone was also boiled several hours with the mixture of sulphuric acid and potassium dichromate used by Remsen[2] in oxidizing paratolylsulphoneamide to parasulphaminebenzoic acid. But this method proved unsuccessful, and the sulphone was recovered unchanged and used in the method finally employed. Chromic acid was ultimately used as an oxidizing agent. Considerable experimenting was done to discover the exact conditions which would give the best yield. The following method was adopted: Five parts of the sulphone are dissolved in the smallest possible quantity of warm glacial acetic acid contained in a flask of convenient size, which is attached to a return condenser. Tne solution is raised nearly to the boiling point, and 8 parts of chromic acid, also dissolved in the least possible amount of cold glacial acetic acid, are added through the inner tube of the condenser in portions of about 10 cc. each. After each addition of the chromic acid solution, the flask is shaken, the temperature being regulated so that the solution just boils. When all the chromic acid has bean added, the mixture is boiled for two hours; the excess of acetic acid is then distilled off, and when the flask has cooled, the paraphenylsulphonebenzoic acid remains as a fine powder, more or less greenish in color from the chromium salts. The contents of the flask is poured into a large porcelain dish and washed several times with hot water. It is bet-

[1] *Loc. cit.* [2] Ann. Chem. (Liebig), **178**, 294.

ter to wash by decantation until only a slight greenish tinge remains, and then wash on the filter-pump, otherwise a trace of chromium salts will persist in remaining in the crystallized product. The acid is then converted into the sodium salt by boiling with sodium carbonate, and the acid reprecipitated by hydrochloric acid.

The acid prepared in this way has, when wet, the appearance of whipped cream, and when dry is a pure white powder. It is soluble in boiling nitrobenzene, but separates out as a crystalline mass; it is soluble in hot glacial acetic acid, from which it crystallizes in small transparent, double wedge-shaped prisms. Both these solvents are difficult to remove from the crystallized product. It is insoluble in absolute ether and in both hot and cold water. The best solvent is hot alcohol (95 per cent.), from which it crystallizes easily in small white prisms. Michael and Adair[1] state that the acid melts above 300°. This is incorrect, as several determinations of the melting point of the crystallized product show conclusively that paraphenylsulphonebenzoic acid melts at 273° uncorr.

Three new salts of this acid were made.

Calcium Salt.—This is made by boiling the acid suspended in water with powdered Iceland spar. Fine white needles separate out of the cooled aqueous solution, which are slightly deliquescent in the air. The following results were obtained on analysis:

0.2346 gram of the salt heated at 155° to constant weight lost 0.0041 gram of H_2O.

	Calculated for $\left(C_6H_4<\begin{matrix}COO\\SO_2\cdot C_6H_5\end{matrix}\right)_2Ca+\frac{1}{2}H_2O$.	Found.
H_2O	1.58	1.74

0.2305 gram dehydrated salt gave 0.0561 gram $CaSO_4$.

	Calculated for $\left(C_6H_4<\begin{matrix}COO\\SO_2\cdot C_6H_5\end{matrix}\right)_2Ca$.	Found.
Ca	7.11	7.15

Barium Salt.—This salt is made by suspending the acid in water and boiling with pure barium carbonate. It crystallizes from the cooled aqueous solution in fine white needles, which show a marked tendency to arrange themselves in sheaves. Analysis gave the following results:

[1] *Loc. cit.*

0.2715 gram air-dried salt when heated at 110° to constant weight lost 0.002 gram H_2O.

	Calculated for $(C_6H_4<^{COO}_{SO_2.C_6H_5})_2Ba+\frac{1}{2}H_2O$.	Found.
H_2O	0.68	0.73

0.2242 gram dehydrated salt gave 0.0784 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COO}_{SO_2.C_6H_5})_2Ba$.	Found.
Ba	20.81	20.57

Sodium Salt.—This salt is made by simply boiling the acid in an aqueous solution of pure sodium carbonate. The solution is filtered, evaporated to dryness, and the residue crystallized from hot alcohol. It crystallizes as fine needles, and resembles the barium salt in its tendency to form sheaf-like clusters. It is slightly efflorescent in the air. The following results were obtained on analysis:

0.1711 gram of the salt dried between filter-paper and heated at 110° to constant weight lost 0.0018 gram H_2O.

	Calculated for $C_6H_4<^{COONa}_{SO_2.C_6H_5}+\frac{1}{2}H_2O$.	Found.
H_2O	1.58	1.05

0.1693 gram dehydrated salt gave 0.0414 gram Na_2SO_4.

	Calculated for $C_6H_4<^{COONa}_{SO_2.C_6H_5}$.	Found.
Na	8.11	7.93

V. Paraphenylsulphonebenzoyl Chloride.

This compound can be made by heating paraphenylsulphonebenzoic acid or its salts with phosphorus pentachloride. It is best prepared from the acid. Equal weights of the powdered acid and dry phosphorus pentachloride are intimately mixed in a flask of convenient size. To this flask is attached a glass tube about 45 cm. long and having two arms of different lengths bent at angles of 110° to the horizontal part of the tube; the shorter arm passes just through the stopper of the flask, while the longer arm reaches to the bottom of a test tube surrounded with ice. The flask is placed in a sulphuric-acid bath, slowly heated to 200° and kept at this temperature for about half an hour. If the operation is conducted slowly, this process changes all the acid into the corresponding acid chlo-

ride, and most of the phosphorus oxychloride distils over into the test-tube. Hydrochloric acid is evolved during almost the whole process. When the operation is over the flask is removed from the bath and allowed to cool. The chloride solidifies at 145°–150° to a brownish amorphous mass. It is softened with a little warm water, transferred from the flask to a mortar, powdered and washed with warm water by decantation. This operation must be repeated several times, otherwise the chloride will retain traces of phosphorus oxychloride, which is difficult to remove from the crystallized product. The chloride is carefully dried and crystallized from hot petroleum ether (boiling point 80°–110°). It is not easily soluble in boiling petroleum ether, but the liquid boiling between these points was found to be the best of several solvents. The yield is about 90 per cent. of the theoretical.

The chloride crystallizes from boiling petroleum ether in fine glistening white plates and sometimes in short white needles, depending upon the method of extraction and rate of crystallization. It is soluble in warm dry benzene, from which it crystallizes in small rhombohedrons, if the liquid is slowly evaporated. It is soluble in boiling absolute ether and crystallizes from this solvent in delicate needles. It is insoluble in petroleum ether boiling between 30° and 50°. The melting-point was found by a Zincke thermometer to be 145.2°–145.8°.

When the chloride is boiled with water the corresponding acid is regenerated and hydrochloric acid is formed. A determination of chlorine by this method gave the following result :

0.1697 gram chloride gave 0.0845 gram AgCl.

	Calculated for $C_{13}H_9SO_3Cl$.	Found.
Cl	12.62	12.31

The chlorine was also determined by the following method : The chloride was heated just to the boiling-point for several hours with a dilute solution of caustic potash and then acidified with dilute nitric acid ; the regenerated acid is filtered off and the chlorine precipitated as usual. By this method the result was :

Cl	12.62	12.42

The chloride is slightly volatile. When 0.0505 gram of the air-dried substance was slowly heated to 137° it lost 0.0043 gram. In accordance with the analysis, general conduct, and method of preparation, this chloride has been given the formula $C_6H_4<^{CO.Cl}_{SO_2.C_6H_5}$.

VI. Paraphenylsulphonebenzamide.

When paraphenylsulphonebenzoyl chloride is treated with an excess of concentrated ammonium hydroxide at the ordinary temperature, and allowed to stand twenty-four hours with occasional stirring, there is no visible change, since both the chloride and the product of the reaction are insoluble in the liquid used. The white powder which finally settles to the bottom of the beaker has much the same appearance as the chloride, but it is insoluble in boiling petroleum ether (boiling point 80°–110°) and also in hot anhydrous ether. From hot alcohol (95 per cent.) it separates out in small transparent acicular crystals, which melt at 242°–243° uncorr.

Analysis for nitrogen by the absolute method and for sulphur by Liebig's method gave the following results:

I. 0.3743 gram substance gave 16.44 cc. = 0.0206 gram nitrogen under standard conditions.

II. 0.3545 gram substance gave 0.3212 gram $BaSO_4$.

	Calculated for $C_{13}H_{11}SO_3N$.	Found. I.	Found. II.
N	5.37	5.55	....
S	12.27	....	12.45

The filtrate from the above method of preparation, when evaporated to dryness, gave nothing but ammonium chloride. The method of preparation together with the analysis show this compound to be the amide corresponding to paraphenylsulphonebenzoyl chloride, and it has been given the following formula: $C_6H_4<^{CO.NH_2}_{SO_2.C_6H_5}$.

VII. Paraphenylsulphonebenzanilide.

This anilide is best made in the following manner: Paraphenylsulphonebenzoyl chloride is dissolved in warm dry benzene contained in an Erlenmeyer flask of convenient size, and an excess of aniline added, drop by drop, with constant shak-

ing. When all the aniline has been added and the mixture shaken for about ten minutes, cold water is added to dissolve the aniline hydrochloride. At this stage the anilide appears as a white gummy mass floating on the surface of the liquid. The mixture is filtered and the anilide washed with warm benzene and finally with cold alcohol. The filtrate, on evaporation to dryness, proved to contain nothing but aniline hydrochloride.

The anilide is soluble in hot alcohol (95 per cent.), but insoluble in boiling petroleum ether (boiling-point 80°–110°), in hot absolute alcohol, boiling caustic soda, and boiling hydrochloric acid. It crystallizes from alcohol in transparent small prisms which melt at 202°–203° uncorr.

Analyses made by the same methods as in the case of the amide (*supra*) gave the following results:

I. 0.2904 gram substance gave 10.43 cc. = 0.01308 gram nitrogen under standard conditions.

II. 0.3073 gram substance gave 0.213 gram $BaSO_4$.

	Calculated for $C_{19}H_{15}SO_3N$.	Found. I.	Found. II.
N	4.16	4.50	....
S	9.48	....	9.52

The method of preparation and analysis show that this compound is the anilide of paraphenylsulphonebenzoyl chloride and hence has the formula $C_6H_4<\begin{matrix}CO.NHC_6H_5\\SO_2.C_6H_5\end{matrix}$.

VIII. Parabenzoyldiphenylsulphone.

The easy and rapid transformation of paratoluenesulphone chloride into paratolylphenylsulphone, as well as the preparation of orthobenzoyldiphenylsulphone from the mixed chlorides and from the high-melting chloride of orthosulphobenzoic acid by means of the Friedel-Crafts reaction led to immediate adoption of this method for the transformation of paraphenylsulphonebenzoyl chloride into parabenzoyldiphenylsulphone.

A method analogous to the one described on page 6 was first used. Five grams of the chloride was dissolved in thirty grams of warm benzene, and the water-bath surrounding the flask which contained the solution was raised to 60°. Upon

the addition of powdered aluminium chloride, little or no action took place; but when the temperature was raised to 70°, hydrochloric acid was rapidly evolved and a dark-red heavy oil settled to the bottom of the flask. Aluminium chloride was added in small portions until no more hydrochloric acid was evolved at 70°, about nine grams in all being added. The temperature was then raised to 80° and kept at this point for five minutes. When the evolution of hydrochloric acid had entirely ceased, the product of the reaction, together with the supernatant benzene and unchanged aluminium chloride, was poured into a large volume of water, and acidified with hydrochloric acid. The reddish oil solidified to a yellowish-brown flakey mass, which encrusted the surface of the liquid after the last traces of benzene had been driven off on the water-bath. It was then washed free from acid with warm water, purified with animal charcoal, and crystallized from hot alcohol (95 per cent).

The method described above gave a good yield of the pure product, but a simpler one was finally adopted. The detailed method is as follows: Ten grams of the chloride is dissolved in twice its weight of warm benzene contained in a small beaker. When the temperature is 70°–75°, from 12 to 15 grams of powdered aluminium chloride is added in three portions; if the action is too vigorous the liquid is allowed to cool below 70°, when the reaction almost ceases. As the operation proceeds, hydrochloric acid is evolved and the product of the reaction settles to the bottom of the beaker as a dark-red oily liquid. The transformation is complete when no more hydrochloric acid is evolved on raising the temperature to the boiling-point of the benzene, the whole operation requiring not more than fifteen minutes. The product is purified and crystallized as described above, the yield being about 90 per cent. of the theoretical.

The substance crystallizes from alcohol in fine white lustrous needles, which, when dry, pack together like felt. They require only one purification with animal charcoal, and, when pure, melt sharply at 143° uncorr. They are slightly soluble in cold and in warm benzene, in warm ether, and very soluble in warm alcohol. They dissolve in warm concentrated

nitric acid and in cold concentrated sulphuric acid, and are recovered unchanged from both. They are not attacked by alcoholic potash even when the substances are boiled together for a day; and they are stable in the air.

The following results were obtained on analysis:

I. 0.1504 gram gave 0.3851 gram CO_2 and 0.06375 gram H_2O.

II. 0.2257 gram gave 0.1524 gram $BaSO_4$.

III. 0.1310 gram gave 0.0908 gram $BaSO_4$.

IV. 0.2797 gram gave 0.2088 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_3$.	Found. I.	II.	III.	IV.
C	70.78	70.37	....	....	....
H	4.35	4.70	....	....	....
S	9.95	....	9.37	9.53	10.26

The determinations of carbon and hydrogen were made by de Roode's modification of the lead chromate method; the first two determinations of sulphur were made by Liebig's method, and the last by the method of Carius.

When orthobenzoyldiphenylsulphone is heated slowly with an excess of caustic potash "the action takes plaee rapidly at 200°–210°, with formation of a yellowish-brown mass. This, when warmed with water, partially dissolves; the residue when separated by filtration and recrystallization from alcohol, gives the characteristic rhombic crystals of diphenylsulphone, melting at 123°–124°, and having the solubility and general properties of that compound. The filtrate treated with hydrochloric acid gives a precipitate of benzoic acid."[1]

Now when parabenzoyldiphenylsulphone is subjected to the same treatment, the results are entirely different. The sulphone was fused twice in a silver crucible, four times in a sealed hard glass tube, and once in a distilling bulb. In all cases the general character of the reaction is the same. Incipient fusion produces a greenish scum on the surface of the molten potash, and at the same time a volatile substance is given off having a pleasant ethereal odor.[2] Attempts were made to obtain the substance giving this odor but they were unsuccessful. When the temperature reaches about 200°–210°, the greenish scum turns to a yellowish-brown porous

[1] Saunders, *Loc. cit.*

[2] This volatilization may be an explanation of the low results obtained in the sulphur determinations by Liebig's method.

mass, which still remains on the surface of the potash. When the fused mass is treated as in the fusion of the ortho compound, there are no traces of either diphenylsulphone or benzoic acid. A variety of results were obtained, even when the fusion was apparently conducted in precisely the same manner. In one instance a substance was obtained which had some properties characteristic of benzoic acid, but it was impure and so small in quantity that it could not be regarded as a real product of the reaction. In two instances a substance was obtained melting at 126°–128° and crystallizing from hot alcohol (95 per cent.) in small transparent flakes, but the amount was too small for identification. In several of the fusions—especially those performed in the sealed glass tube—a white powder was obtained from an alcoholic solution of that portion of the fused mass insoluble in water. This powder melted at about 90°, but was impure and was not further investigated.

In view of these facts it must be concluded that when parabenzoyldiphenylsulphone is fused with caustic potash, it does not decompose into benzoic acid and diphenylsulphone, differing markedly in this respect from the corresponding ortho compound.

IX. Derivatives of Parabenzoyldiphenylsulphone.

The method of preparation, the properties, and analysis of this compound show that it must have the structural formula indicated by $C_6H_4<^{CO.C_6H_5}_{SO_2.C_6H_5}$. This being the fact, we should naturally expect it to yield a hydrazone with phenylhydrazine, and an oxime, or oximes, with hydroxylamine, owing to the presence of the carbonyl group, CO, in the compound. Both the hydrazone and the oxime were made.

1. *Hydrazone.*

When equal quantities of parabenzoyldiphenylsulphone and phenylhydrazine, dissolved in a convenient quantity of alcohol, are boiled on the water-bath with a return condenser for three days, lemon-yellow, lustrous needles separate out of the cooled alcohol. These needles when washed free from phenylhydrazine and recrystallized from hot alcohol (95 per cent.) melt

sharply at 184° uncorr. When boiled a day with concentrated hydrochloric acid, the substance splits up into phenylhydrazine and the original substance. The beautiful yellow color is not removed by animal charcoal, and the substance is stable in the air.

Analysis gave the following results:

I. 0.0518 gram gave 0.0288 gram $BaSO_4$.

II. 0.18775 gram gave 0.496 gram CO_2 and 0.0802 gram H_2O.

III. 0.1953 gram gave 0.5191 gram CO_2 and 0.0970 gram H_2O.

IV. 0.1873 gram gave 0.4943 gram CO_2 and 0.0844 gram H_2O.

V. 0.1420 gram gave 8.05 cc. = 0.01009 gram nitrogen under standard conditions.

	Calculated for $C_{25}H_{20}SO_2N_2$.	Found. I.	II.	III.	IV.	V.
S	7.77	7.64	....	....	....	....
C	72.78	....	72.04	72.48	72.00	....
H	4.86	....	4.75	5.52	5.00	....
N	6.83	....	....	....	....	7.11

The sulphur was determined by the method of Carius, the nitrogen by the absolute method, and the carbon and hydrogen by de Roode's modification of the lead chromate method.

The preparation, general conduct, and analysis of this compound show it to be paradiphenylsulphonebenzoylhydrazone. Its structural formula is probably:

$$C_6H_4 < \begin{matrix} SO_2.C_6H_5 \\ C.C_6H_5 \\ \| \\ N.NH.C_6H_5 \end{matrix}$$

The alcoholic filtrate obtained in the preparation of the first specimens of this hydrazone was evaporated to dryness, and in each case a reddish crystalline mass resulted. This residue was at first thought to be the hydrazone itself. It proved however to be something entirely different. It was soluble in hot water, cold methyl alcohol, hot ordinary ether, and in boiling petroleum ether (boiling point 80°–110°). Its color when crystallized was a faint yellow and was not removed by animal charcoal. By crystallization from different solvents

two kinds of crystals were obtained — small plates and needles both melting at 125°–127°. Both kinds of crystals were split up into phenylhydrazine and acetic acid in the following manner: The crystals were boiled with concentrated hydrochloric acid for a day, and into this solution, made alkaline with caustic potash, steam was passed; an oil distilled over with the steam, which had the odor of phenylhydrazine and reduced Fehling's solution. The alkaline liquid into which the steam was passed was evaporated to dryness, and in the residue acetic acid was detected by the ethyl acetate method.

The properties and reactions of this substance—particularly its decomposition into phenylhydrazine and acetic acid—suggested its identity with acetylphenylhydrazine. A sample of pure acetylphenylhydrazine was made according to the method of Fischer.[1] It melted at 128° and had all the properties of the residue mentioned above, including solubility, crystal forms, reducing power, etc. It also was decomposed by the method mentioned above into acetic acid and phenylhydrazine. There seems to be little doubt that the substance in question was acetylphenylhydrazine. The evidence, however, is not conclusive. The substance was not obtained in every instance, in fact only in the first two or three experiments, and then not in very large quantities. Not enough was obtained in a condition pure enough for analysis. While it seems plausible that from some deep-seated cause the alcohol used in the experiment may have been oxidized to acetic acid, and that the acetic acid may have formed acetylphenylhydrazine with the excess of phenylhydrazine present, still the conclusion must be drawn that if acetylphenylhydrazine is formed as a secondary product when parabenzoyldiphenylsulphone is treated with phenylhydrazine in alcoholic solution, it is formed only as the result of some unknown and perhaps accidental cause.

2. *Oxime.*

The oxime corresponding to parabenzoyldiphenylsulphone was first made by boiling an alcoholic solution of the sulphone with a slight excess of an aqueous solution of hydroxylamine hydrochloride to which the calculated amount of sodium car-

[1] Ann. chem.,(Liebig), **190**, 129.

bonate had been added. It was found necessary to continue the action for three days in order to transform all the sulphone into the oxime. By this method a mixture was obtained which by repeated crystallizations from hot alcohol (95 per cent.) finally yielded thin irregular leaflets melting at 201° uncorr, with evolution of a gas, and small white needles melting at 154° uncorr. This method was abandoned for one similar to that used by Auwers[1] for the preparation of the benziloximes. The method finally adopted is as follows: Eleven parts of parabenzoyldiphenylsulphone are dissolved in a slight excess of hot ordinary alcohol, and to this hot solution there is added a clear aqueous solution of 5 parts of hydroxylamine hydrochloride. If the solution is not clear, alcohol is added until the hot solution is perfectly clear. To this solution there is added a filtered aqueous solution of 8 parts of caustic soda. The clear liquid is now boiled for not less than two hours on the water-bath, filtered, if necessary, while hot, and acidified with hydrochloric acid. The oxime which settles out as a white powder is filtered, washed with cold water, dried at 110°, and recrystallized from hot alcohol (95 per cent). The crystals obtained by this method are always the thin irregular leaflets melting at 201° uncorr. When boiled for a day with concentrated hydrochloric acid they split up into hydroxylamine and the original substance. They are insoluble in cold water and the best crystals come from hot alcohol.

Analysis gave the following results:

I. 0.1986 gram gave 0.4872 gram CO_2 and 0.083 gram H_2O.

II. 0.1978 gram gave 0.4857 gram CO_2 and 0.0809 gram H_2O.

III. 0.1608 gram gave 0.1208 gram $BaSO_4$.

IV. 0.2393 gram gave 8.22 cc. = 0.0103 gram nitrogen under standard conditions.

	Calculated for $C_{18}H_{10}SO_3N$.	Found. I.	II.	III.	IV.
C	67.63	66.92	66.97	....	....
H	4.46	4.64	4.48	....	....
S	9.55	....	....	9.70	....
N	4.16	....	....	....	4.33

The determinations were made by the same methods as in the analysis of the hydrazone.

[1] Ber. d. chem. Ges., **22**, 604.

The preparation, general conduct, and analysis of this compound leave no doubt that it is an oxime of parabenzoyldiphenylsulphone and has one of the two structural formulas represented thus :

$$C_6H_5SO_2.\overset{\text{I.}}{C_6H_4}.C(=N.OH).C_6H_5 \quad \text{or} \quad C_6H_5.SO_2.\overset{\text{II.}}{C_6H_4}C(=HO.N).C_6H_5$$

The needles melting at 154° (see above) were obtained only once, and then by the first method of preparation. The conditions under which they were made were reproduced as far as possible, since they were thought to be an isomeric modification of the oxime isolated, but to no avail. The conditions and methods were also modified in various ways, but no trace of an isomer could be obtained after many trials. The work on this possible isomeric form was abandoned from lack of material.

The comparative ease with which the oxime and hydrazone of parabenzoyldiphenylsulphone are made, together with the fact that the methods of preparation vary somewhat from those used by Saunders in his ineffectual attempt to prepare the oxime and the hydrazone of *ortho*benzoyldiphenylsulphone, suggested the possibility of obtaining a reaction by the methods used in the case of the para compound. Accordingly, some orthobenzoyldiphenylsulphone was purified and recrystallized till it had a constant melting-point (187°, uncorr.). It was then boiled with an equal weight of phenylhydrazine in alcoholic solution. At the end of three days the original substance was recovered. At the end of five days' continuous boiling the orthobenzoyldiphenylsulphone crystallized out of the cooled alcohol. The alcoholic filtrate was evaporated nearly to dryness, and yielded nothing but phenylhydrazine.

Another portion of the orthosulphone was boiled in alcoholic solution with the proper proportions of hydroxylamine hydrochloride and caustic soda under the same conditions as those used for the preparation of the oxime of the parasulphone. At the end of two hours' boiling the original substance settled out ; the action was continued for nine and a half hours and at the end of that time the orthobenzoyldiphenylsulphone crystallized out of the solution when cooled.

It had the same crystal form and the same melting-point as the original substance used. These experiments confirm the work of Saunders, who obtained neither the oxime nor the hydrazone.

Conclusion.

The results of this investigation may be briefly summarized as follows:

1. Paratoluenesulphone chloride, by means of the Friedel-Crafts reaction, passes easily into paratolylphenylsulphone.

2. This sulphone can be best oxidized by chromic acid to paraphenylsulphonebenzoic acid, which forms well characterized salts.

3. When heated to 200° (under proper conditions) with phosphorus pentachloride, this acid forms an acid chloride having the formula

$$C_6H_4<\begin{matrix}CO.Cl\\SO_2.C_6H_5\end{matrix}.$$

4. Paraphenylsulphonebenzoyl chloride when treated with concentrated ammonium hydroxide at the ordinary temperature forms are amide having the constitution

$$C_6H_4<\begin{matrix}CO.NH_2\\SO_2.C_6H_5\end{matrix}.$$

And when treated with an excess of aniline in benzene solution, it yields an anilide of the formula

$$C_6H_4<\begin{matrix}CO.NHC_6H_5\\SO_2.C_6H_5\end{matrix}.$$

5. A third compound was obtained from paraphenylsulphonebenzoyl chloride, by means of the Friedel-Crafts reaction, which proved to be parabenzoyldiphenylsulphone, a compound analogous to the compound obtained by Saunders from the chlorides of orthosulphobenzoic acid by the same reaction. It has the constitutional formula represented by

$$C_6H_4<\begin{matrix}CO.C_6H_5\\SO_2.C_6H_5\end{matrix},$$

6. This compound, unlike the corresponding ortho compound, does not decompose into benzoic acid and diphenylsulphone when fused with caustic potash. On the other hand, it does yield a hydrazone, having the constitution

$$C_6H_4 < \begin{matrix} SO_2.C_6H_5 \\ C.C_6H_5 \\ \| \\ N.NH.C_6H_5 \end{matrix} ,$$

by prolonged treatment with phenylhydrazine. It likewise gives with hydroxylamine an oxime having all the properties of that class of compounds. This has one of the two formulas

I. $C_6H_5.SO_2.C_6H_4.C(=N.OH).C_6H_5$ II. $C_6H_5.SO_2.C_6H_4.C(=HO.N).C_6H_5$.

REMARKS.

The six compounds and three additional salts, isolated in this investigation, together with the two compounds made by Michael and Adair, form an unbroken series. Individually, each member has the properties of its class. As a series, it exhibits one remarkable property *viz.*, the stability of the phenylsulphone group,—$SO_2.C_6H_5$. It is not attacked by aluminium chloride, phosphorus pentachloride, concentrated ammonia, aniline, phenylhydrazine, and hydroxylamine under the most favorable conditions. This group remains intact throughout all the transformations from paratolylphenylsulphone through the acid to the chloride, amide, and anilide on one hand, and through the chloride to parabenzoyldiphenylsulphone, its hydrazone and oxime on the other.

Biographical.

The writer was born in Pawtucket, R. I., September 18, 1867. He was educated and prepared for college in the public schools of that city. He entered Brown University in 1886 and received the degree of Ph.B. at the end of a regular course of four years. Immediately after graduation he was appointed instructor in Physical Science in the Pawtucket high school and also instructor in chemistry at Brown University—arrangements being made whereby the combined work could be done. He received the degree of A. M. from Brown University in 1891. The year 1891–92 was spent in teaching the physical sciences in the high school above mentioned. He entered Johns Hopkins University in 1892, where he remained three consecutive years, pursuing chemistry as his principal subject and mineralogy and German as his subordinate subjects.